Structure of the Triphenyl Phosphate–Boron Trichloride Adduct

By M. L. Levin

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802, USA

J. W. Fieldhouse

The Firestone Tire and Rubber Company Laboratories, Akron, Ohio 44317, USA

and H. R. Allcock*

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802, USA

Abstract. $C_{18}H_{15}O_4P \cdot BCl_3$, monoclinic, $P2_1/c$, $a = 9\cdot194$ (5), $b = 20\cdot293$ (15), $c = 11\cdot488$ (5) Å, $\beta = 108\cdot81$ (4)°, $Z = 4$, $D_m = 1\cdot40$, $D_c = 1\cdot45$ Mg m^{-3}, $R = 0\cdot041$ for 1637 reflections. The structure involves coordination between the phosphoryl O and the B atom.

Introduction. The adduct formed between triphenyl phosphate and boron trichloride is an initiator for the polymerization of hexachlorocyclotri(phosphazene), $(NPCl_2)_3$, to poly(dichlorophosphazene), $(NPCl_2)_n$ (Fieldhouse & Graves, 1981). The adduct was first reported by Frazer, Gerrard & Patel (1960) who proposed the structure $(PhO)_3P=O \cdot BCl_3$ on the basis of infrared evidence. However, in principle, other modes of linkage are also possible including an attachment of the BCl_3 unit to one of the dicoordinate O atoms of the organophosphate component (Waddington & Klanberg, 1960; Baaz, Gutmann & Huber, 1960; Gerrard, Mooney & Willis, 1961; Waddington & Peach, 1962; Finch, Gardner & Sen Gupta, 1966; Dillon & Waddington, 1972).

The adduct was prepared by allowing a homogeneous solution of triphenyl phosphate in cyclohexane to react with one equivalent of gaseous boron trichloride at 318–328 K. The precipitate was filtered off in a dry atmosphere to give the crude adduct in 96% yield. Crystals, m.p. 366–367 K (lit. 359–363 K; Frazer, Gerrard & Patel, 1960), suitable for X-ray analysis were obtained from carbon tetrachloride solution. The dimensions of the crystal used for data collection were $0\cdot3 \times 0\cdot4 \times 0\cdot4$ mm.

Data were collected with the use of an Enraf–Nonius CAD-4 diffractometer using graphite-monochromated Mo $K\alpha$ radiation. A preliminary test set of 60 reflections indicated systematic absences of $h0l$ for $l = 2n + 1$ and of $0k0$ for $k = 2n + 1$ which were

consistent with the space group $P2_1/c$. A least-squares refinement of the 2θ values for 25 centered reflections gave the cell dimensions and indicated a monoclinic lattice. The observed volume of 2029 (4) Å^3 is consistent with $Z = 4$ for a calculated density of $1\cdot45$ Mg m^{-3} (observed $1\cdot40$ Mg m^{-3}). A $\theta/2\theta$ scan technique was used for all reflections for which $0\cdot01 \leq 2\theta \leq 60°$. From a total of 6308 unique reflections measured, 1637 were considered observed with $I \geq 3\sigma(I)$. The low number of observed reflections was later attributed to a slight misalignment of the X-ray tube and/or monochromator.

Lorentz and polarization corrections were applied in the determination of structure amplitudes. No absorption correction was considered necessary. The atomic scattering factors used were those of Cromer & Waber (1974) and the anomalous-dispersion correction coefficients were those of Cromer (1974).

The structure was solved by direct methods using *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1978). The phase set with the highest absolute figure of merit was used to generate an E map from which the positions of all nonhydrogen atoms except for one C atom were evident. A subsequent difference synthesis located the missing C atom. Refinement was carried out by the full-matrix least-squares method. Final anisotropic refinement of non-hydrogen atoms with B_{iso} fixed at $4\cdot0$ Å^2 for H atoms gave $R = 0\cdot041$ and $R_w = 0\cdot037$ with an e.s.d. of an observation of unit weight of $1\cdot62$; $R = \sum ||F_o| - |F_c||/\sum |F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$, $w = 1/\sigma(F_o)^2$. The final difference map revealed no residual electron density greater than $0\cdot123$ e Å^{-3}. The atomic positional parameters are listed in Table 1.†

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† Lists of structure factors, anisotropic thermal parameters, bond lengths, and bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36803 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* To whom correspondence should be addressed.

Table 1. *Final positional coordinates with e.s.d.'s in parentheses and equivalent isotropic thermal parameters* (Å^2)

$B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i . \mathbf{a}_j$. The H atoms were assigned a B_{iso} value of $4.0\ \text{Å}^2$.

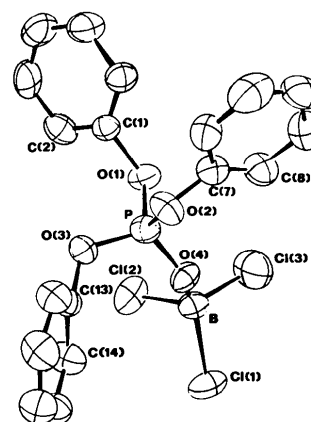|	x	y	z	B_{eq}
Cl(1)	0.4113 (1)	0.19223 (7)	0.4544 (1)	5.2
Cl(2)	0.5539 (1)	0.20144 (7)	0.7295 (1)	5.1
Cl(3)	0.5809 (1)	0.07660 (7)	0.5970 (1)	5.6
P	0.2470 (1)	0.11372 (6)	0.7143 (1)	3.4
O(1)	0.3710 (3)	0.0834 (1)	0.8240 (2)	3.6
O(2)	0.1025 (3)	0.0701 (1)	0.6729 (3)	3.8
O(3)	0.1924 (3)	0.1778 (1)	0.7576 (2)	3.5
O(4)	0.3111 (3)	0.1216 (1)	0.6105 (2)	3.1
C(1)	0.3672 (4)	0.0771 (2)	0.9467 (4)	3.0
C(2)	0.4370 (5)	0.1238 (2)	1.0293 (4)	4.4
C(3)	0.4444 (5)	0.1148 (2)	1.1512 (4)	5.5
C(4)	0.3817 (5)	0.0602 (2)	1.1833 (4)	5.2
C(5)	0.3124 (5)	0.0139 (2)	1.0985 (4)	4.9
C(6)	0.3032 (5)	0.0222 (2)	0.9766 (4)	4.1
C(7)	0.0958 (4)	0.0013 (2)	0.6592 (4)	3.4
C(8)	0.1996 (5)	−0.0333 (2)	0.6207 (4)	4.0
C(9)	0.1824 (5)	−0.1004 (2)	0.6096 (4)	5.1
C(10)	0.0649 (6)	−0.1314 (2)	0.6355 (5)	5.7
C(11)	−0.0360 (5)	−0.0959 (3)	0.6728 (4)	6.1
C(12)	−0.0232 (5)	−0.0289 (2)	0.6853 (4)	4.6
C(13)	0.0884 (4)	0.2223 (2)	0.6748 (4)	3.1
C(14)	0.1455 (4)	0.2687 (2)	0.6171 (4)	4.3
C(15)	0.0451 (5)	0.3122 (2)	0.5404 (4)	4.9
C(16)	−0.1083 (5)	0.3076 (2)	0.5214 (4)	5.4
C(17)	−0.1625 (4)	0.2603 (3)	0.5799 (4)	5.1
C(18)	−0.0656 (4)	0.2164 (2)	0.6582 (4)	4.1
B	0.4603 (5)	0.1472 (3)	0.5991 (4)	3.3
H(C2)	0.483 (3)	0.158 (2)	1.012 (3)	
H(C3)	0.498 (3)	0.148 (2)	1.206 (3)	
H(C4)	0.388 (3)	0.054 (2)	1.265 (3)	
H(C5)	0.273 (3)	−0.025 (2)	1.121 (3)	
H(C6)	0.251 (3)	−0.010 (2)	0.916 (3)	
H(C8)	0.277 (3)	−0.009 (2)	0.598 (3)	
H(C9)	0.251 (3)	−0.125 (2)	0.581 (3)	
H(C10)	0.069 (3)	−0.177 (2)	0.628 (3)	
H(C11)	−0.105 (3)	−0.114 (2)	0.687 (3)	
H(C12)	0.089 (3)	0.002 (2)	1.289 (3)	
H(C14)	0.255 (3)	0.271 (2)	0.636 (3)	
H(C15)	0.085 (3)	0.341 (2)	0.502 (3)	
H(C16)	−0.173 (3)	0.340 (2)	0.465 (3)	
H(C17)	−0.265 (3)	0.261 (2)	0.576 (3)	
H(C18)	−0.105 (3)	0.185 (2)	0.700 (3)	

Fig. 1. Perspective view of triphenyl phosphate–boron trichloride. Thermal ellipsoids for non-hydrogen atoms represent 50% probability.

Table 2. *Bond distances* (Å) *and angles* (°)

Cl(1)–B	1.821 (4)		P–O(4)	1.499 (2)
Cl(2)–B	1.834 (5)		O(1)–C(1)	1.428 (4)
Cl(3)–B	1.818 (5)		O(2)–C(7)	1.403 (4)
P–O(1)	1.529 (2)		O(3)–C(13)	1.432 (4)
P–O(2)	1.538 (2)		O(4)–B	1.511 (5)
P–O(3)	1.534 (2)			

O(1)–P–O(2)	111.35 (15)		Cl(1)–B–Cl(2)	110.92 (25)
O(1)–P–O(3)	108.00 (15)		Cl(1)–B–Cl(3)	110.84 (24)
O(1)–P–O(4)	108.50 (14)		Cl(1)–B–O(4)	106.58 (27)
O(2)–P–O(3)	104.36 (15)		Cl(2)–B–Cl(3)	110.97 (24)
O(2)–P–O(4)	109.61 (15)		Cl(2)–B–O(4)	109.54 (27)
O(3)–P–O(4)	115.01 (15)		Cl(3)–B–O(4)	107.85 (29)

1965) and results in less distortion of the tetrahedral environment about P.

The long B—O(4) coordinative bond, and the lengthening of the B—Cl bonds relative to free BCl_3, can be attributed to primary inductive effects. The geometry of this molecule is consistent with those of other electron-pair σ-donor—σ-acceptor complexes (Hoard, Geller & Cashin, 1951; Geller & Hoard, 1951; Brändén, 1963; McGandy & Eriks, 1961).

Discussion. An *ORTEP* drawing (Johnson, 1965), with the atomic-numbering system, is shown in Fig. 1. Pertinent bond distances and angles are given in Table 2. The C—C bond distances vary between 1.348 (5) and 1.392 (6) Å and the bond angles within the phenyl rings range from 117.39 (4) to 123.13 (4)°. These rings are planar with a mean deviation of the atoms from the best least-squares planes of 0.002 Å.

The molecule possesses distorted tetrahedral centers about P and B, bridged by a common O atom. The P—O(4) bond distance for $(PhO)_3P=O.BCl_3$ is considerably longer than the 1.432 Å found for un-complexed triphenyl phosphate (Svetich & Caughlan,

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Structure of 2,2',6,6'-Tetranitro-4,4'-isopropylidenediphenol

BY J. L. WANG, C. P. TANG AND Y. J. CHEN

Chung Shan Institute of Science and Technology, PO Box 1–4, Lung Tan, Taiwan 352

Abstract. $C_{15}H_{12}N_4O_{10}$, $M_r = 408.28$, monoclinic, $C2/c$, $a = 17.202$ (1), $b = 9.477$ (1), $c = 11.263$ (1) Å, $\beta = 107.0$ (1)°, $Z = 4$, $D_c = 1.544$, $D_m = 1.535$ g cm^{-3}. The structure was solved by direct methods and refined by full-matrix anisotropic least squares to a final R of 0.068 for 1590 reflections. The molecule has C_2 symmetry. The dihedral angle between the two phenyl-ring planes is 63.9 (5)°. The —OH group forms an ordered intramolecular hydrogen bond with one of the two neighboring nitro groups. The other nitro group is rotated through 46.5 (3)° from coplanarity with the phenyl ring.

Introduction. In the title compound each hydroxy group lies between two nitro groups.
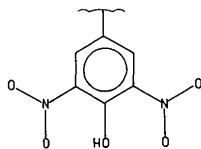
The present structure analysis was undertaken to study the intramolecular hydrogen bonds in this symmetrical molecule.

The compound was synthesized according to du Pont de Nemours & Co. (1937). Yellow crystals were crystallized from benzene solution. Intensity data were collected at room temperature using a θ–2θ scan

technique on a CAD-4F four-circle automatic diffractometer with graphite-monochromatized Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å). No time-decay correction was made, since three monitoring reflections were measured periodically which showed only slight random fluctuations. 1622 independent reflections ($2\theta \leq 140°$) were corrected for Lorentz and polarization effects, but not for absorption ($\mu = 11.69$ cm^{-1}). 1590 reflections had $|F_o| > 2\sigma|F_o|$.

The structure was solved by *MULTAN* (Germain, Main & Woolfson, 1971). The E map revealed the molecular structure and confirmed the space group $C2/c$. The non-hydrogen-atom coordinates with isotropic thermal parameters were refined by full-matrix least-squares techniques. The phenyl H atoms were then inserted into chemically reasonable positions and the methyl and hydroxyl H atoms were located on difference maps. The final cycle of the refinement with anisotropic thermal parameters for all non-hydrogen atoms, except for the central C(7), yielded R and R_w values of 0.068 and 0.03, respectively, where $R = \sum ||F_o| - |F_c||/\sum |F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.* The weighting scheme of Stout &